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Novel Techniques of Carbon Capture Monitoring: Geochemical Studies Based on CO_2-Brine-Rock Interactions for CO_2 Sequestration

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Abstract

This paper presents innovative combinational petrophysical approaches to address geochemical interactions for CO_2 sequestration. Previous studies utilizing batch reactions and in-situ visualization with a Computerized tomography (CT) scanner showed trends and advancements in lab and simulation scale research that can be extended to provide a comprehensive understanding of various aspects of reactive transport mechanisms, including permeability, porosity, CO_2 dry-out effects, and mineralogical changes. This research focuses on CO_2 MPD (mineralization, precipitation, and dissolution) and explores alterations in petrophysical properties during core flooding and static batch reactors in reservoir rocks. Geo-electrical properties, including complex conductivity, dielectric dispersion, and zeta potential, provide methods to characterize and evaluate geochemical reaction sites and to apply novel techniques of carbon capture monitoring.

Our novel research is based on static batch reactor with resistivity monitoring using PLS 400 (Petrophysical Laboratory System) to establish CO_2/rock equilibrium and reaction progress. Dielectric permittivity and dielectric dispersion are used to characterize the reservoir rocks before and after CO_2 geochemical interactions. We monitored how these changes occurred based on dielectric permittivity and dielectric constant after complete exposure of $scCO_2$ as a function of time.

We validated the MPD changes by ISSM (in situ saturation monitoring) of CO_2 using industrial CT and micro CT scanners. We used thin section measurements and image-registered micro CT scanning to obtain mineralogy and capture pore and matrix features to identify details of the changes in rock geochemistry. We aim to advance future monitoring of carbon storage technology in a significant way using our innovative methodology. We believe that MPD monitoring is a crucial item for addressing the environmental impact of net zero technology.

Our novel research concept is based on static batch reactor with resistivity monitoring using PLS 400 and dielectric measurements to understand geochemical reactions between CO_2 -rock-brine. These are

used to characterize the reservoir rocks before and after CO_2 geochemical reactions. This type of novel approach is needed for advancing the overall goal of carbon management worldwide.

Introduction

In October 2024, the Department of Energy (DOE) announced an investment of $518 million for strengthening national infrastructure to ensure the safe and permanent storage of carbon pollution, as reported by the Office of Fossil Energy and Carbon Management. This initiative is part of a broader effort to develop new and innovative techniques for monitoring carbon capture, which is crucial for mitigating the impacts of global warming and climate change.

Khan, M., Siddiqui, S., and Thakur, G. (2024) emphasize in their recent study the critical role of geochemistry in understanding the processes of mineralization, precipitation, and dissolution (MPD) in CO_2-brine-rock interactions. They argue that geochemical and mineralogical exposure to supercritical CO_2 ($scCO_2$) is essential for capturing long-term CO_2 sequestration, providing insights into the stability and behavior of CO_2 stored in geological formations. According to (Zhao *et al.*, 2014), CO_2 sequestration involves four primary trapping mechanisms: mineral trapping, solubility trapping, residual trapping, and structural/stratigraphic trapping.

This study experimentally investigates and visualizes MPD processes using the Petrophysical Laboratory System (PLS 400) equipment for long-term CO_2 storage. The study further incorporates industrial and micro CT scanning techniques to observe the physical changes in rock samples, with results validated using dielectric impedance measurements. These methodologies collectively offer a comprehensive approach to understanding CO_2 sequestration and its long-term effects on geological formations.

Methodology

The methodology of this study is organized into five distinct sections:

a) Porosity and Permeability Measurements: The Ultra-Pore and Ultra-Perm 600 instruments were employed to measure the porosity and permeability of the carbonate samples, providing essential data on the pore network and flow characteristics.

b) Thin Section Imaging: Thin section images were obtained using the Zeiss Imager.Z2m, capturing the microstructural features of the samples before and after exposure to $scCO_2$. These images were instrumental in visualizing any changes in the pore structure due to CO_2 sequestration.

c) Analytical Techniques: X-ray diffraction (XRD) and scanning electron microscopy (SEM) were utilized to examine the mineralogical and grain structure changes within the samples before and after the 30-day CO_2 exposure. These techniques offered insights into the alterations at the microscopic and molecular levels.

d) Resistivity Monitoring: The PLS 400 system was used to monitor resistivity changes throughout the 30 days of CO_2 storage. Four cells, functioning as static batch reactors, contained 1.25-inch plugs of Indiana limestone. To further validate geochemical changes by dielectric measurements, an FF20 YXLON industrial CT scanner and an Xradia 510 Versa (Zeiss) micro CT scanner were employed for high-resolution imaging of the samples.

e) Static Batch Reactor Exposure: Cutting samples of approximately ½ cm were placed in a static batch reactor and exposed to $scCO_2$ and brine to assess pore structure and mineral composition changes. These

alterations were then validated through SEM and XRD analysis, focusing on monitoring the effects of mineral dissolution and CO_2 saturation.

For this study, a 12-inch-long core of Indiana limestone core with a diameter of 1-½ inch was obtained and then cut into four 1.25-inch-long plugs, as depicted in Figure 1. The brine used for the experiments had a salinity of 15 weight percent, representative of conditions found in Permian Basin reservoirs.

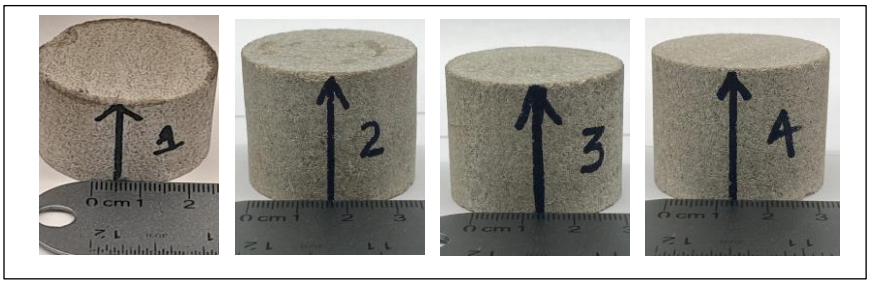


Figure 1. The Indiana limestone samples 1 to 4 which are used for the PLS 400 experiments for CO_2 sequestration.

Figure 2 illustrates the cutting samples, each measuring approximately ½ cm in size, used in the static batch reactors to assess the long-term effects of CO_2 storage. These samples were exposed to $scCO_2$ and brine for 30 days, with the dry weight of the samples recorded in grams to monitor any potential changes during the exposure period. Figure 3 represents the static batch reactor setup, as previously described for the cutting samples in Figure 2. One end of the reactor tubing is connected to a CO_2 gas cylinder, facilitating the injection of $scCO_2$ into the system for controlled exposure. This setup allows for the simulation of CO_2 sequestration conditions and enables monitoring of the effects on the rock samples over the specified period.

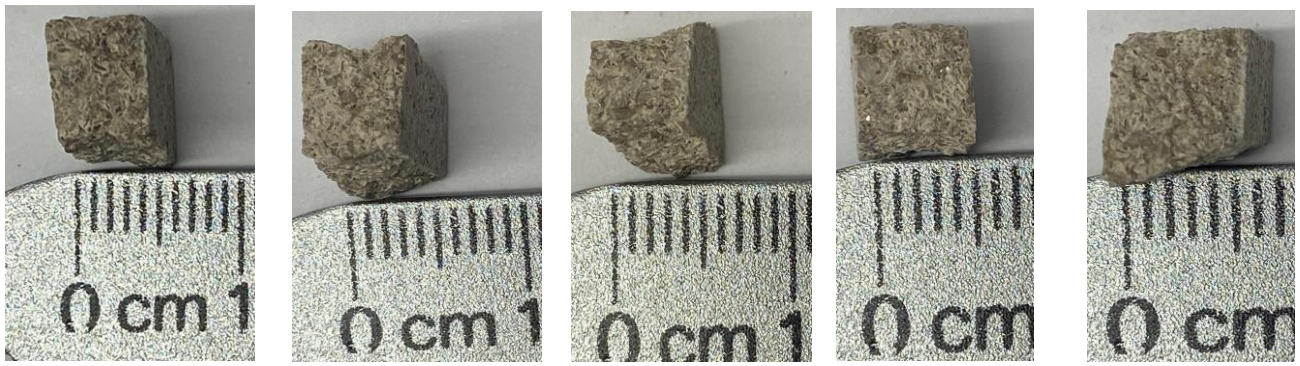


Figure 2. Shows the cutting dry samples for static batch reactor experiments for geochemical reactions before exposure to the $scCO_2$ and brine.

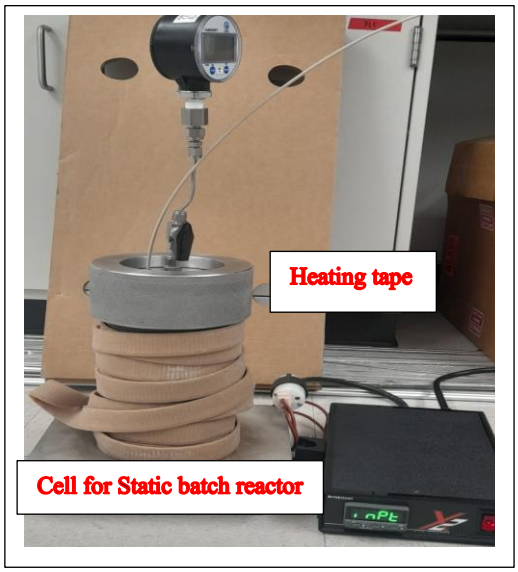
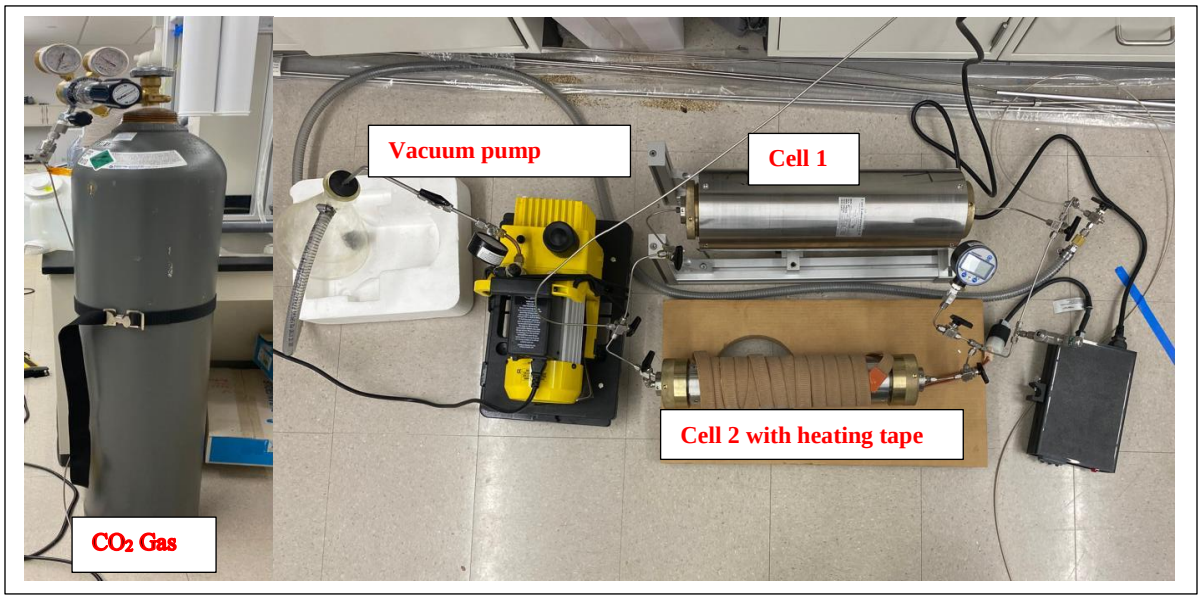


Figure 3. Static Batch Reactors for CO_2-Brine-Rock Interactions During a 30-Day CO_2 Sequestration Experiment.

To prepare $scCO_2$, a temperature of 140 °F and a pressure of 1500 psi were used in this study. (Yee *et al*., 2023) reported using 55 °C and 23.8 MPa for the static batch reactor to expose CO_2 brine under geological sequestration conditions in Cedar Keys-Lawson carbonate samples. The experimental setup for the preparation of scCO2 is illustrated in Figure 4a, while Figure 4b outlines the long-term monitoring of $scCO_2$ using the PLS 400 to measure in situ resistivity. This novel approach allows for the visualization of how resistivity evolves during 30 days of CO_2 storage in carbonate rocks and resistivity measurements for CO_2 monitoring. (Adebayo *et al*., 2017) demonstrated that resistivity logs are reliable for monitoring CO_2 sequestration in carbonate saline reservoirs. Additionally, laboratory experiments have shown that the resistivity of sandstone is significantly affected by the displacement of brine by CO_2, with Archie's equation commonly used to estimate CO_2 saturation. However, it is crucial to acknowledge the limitations of Archie's equation, mainly when applied to heterogeneous reservoirs, as it may not fully account for complex reservoir characteristics (Nakatsuka *et al*., 2010).



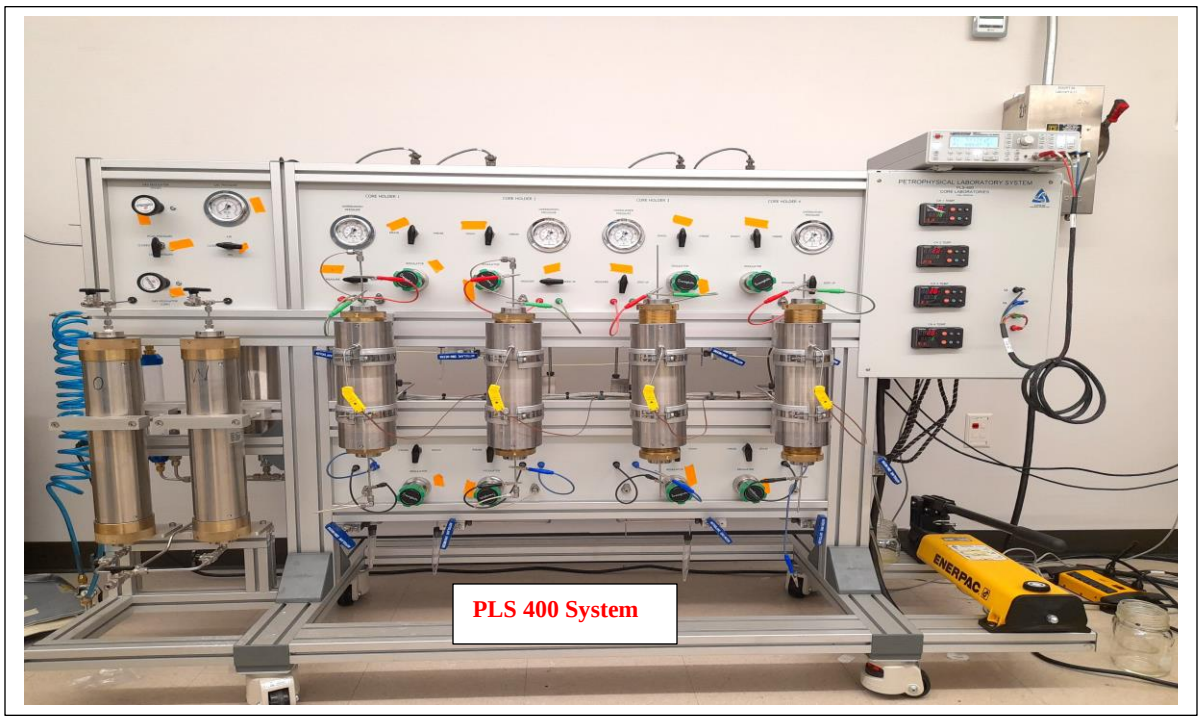


Figure 4a. shows the procedure for generating scCO2, and Figure 4b. illustrates the PLS 400 system for in situ resistivity monitoring setup for 30 days of CO2 storage.

The dielectric measurement, specifically the dielectric constant, presents a novel and compelling approach for validating geochemical and mineralogical alterations within reservoir rocks. This method effectively characterizes the vuggy and matrix pores in carbonate reservoirs before and after $scCO_2$ sequestration, as demonstrated in the tool shown in Figure 5. Additionally, a recent study investigates the key physicochemical and dielectric properties of basalt and silica sites contaminated by CO_2, which results from CO2 sequestration projects. This further underscores the potential of the dielectric measurement technique as a valuable tool for understanding the effects of CO_2 injection and monitoring long-term storage in subsurface environments (Rabiu, K., Abidoye, L., and Das, D. 2020).

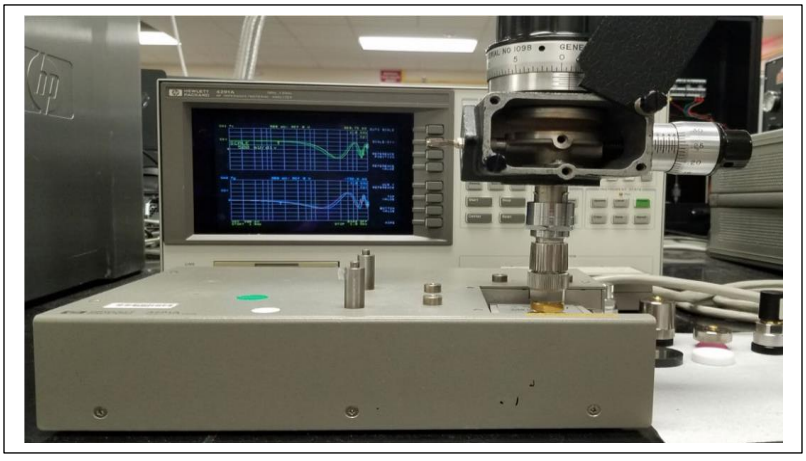


Figure 5. Dielectric Impedance measurement system

Results

The permeability of all four core plugs of limestone ranges from 1.5 to 1.8 mD, with a 3% error. The porosity, dry weight, length and diameter values of core sample limestone plugs are presented in Table 1. Subsequently, all samples (1 to 4) were scanned using both the YXLON industrial CT scanner and the Xradia micro CT scanner. These scans included both the dry samples and those exposed to $scCO_2$ for 30 days in the PLS 400 system. Changes were observed in relation to in situ resistivity monitoring, with a focus on geochemical and mineralogical alterations. Figures 6a, 6b, and 6c display the micro CT scans of dry Sample 2. Figure 6a shows the full image of the dry Sample 2 plug, while Figure 6b shows slice 1327 out of 2034 of dry sample 2, and Figure 6c shows slice 975 out of 2034 of dry sample 2. Figures 7a and 7b present the industrial CT scan images of Sample 3, a limestone plug. Figure 7a shows the entire plug of dry Sample 3, while Figure 7b shows slice 1132 out of 1762 of dry Sample 3. All these images were captured before exposure to CO_2 in the PLS 400 system. Figure 8 shows the industrial CT scan image of cutting sample 2, where the black spots represent pores and the colored spots indicate grains or rock.

Table 1 (Shows porosity, length, diameter and dry weight of core plugs (limestone))

Samples no.	**Porosity (%)**	**Dry weight (gm)**	**Length (cm)**	**Diameter (cm)**
Sample 1	11.729	82.216	3.205	3.739
Sample 2	11.464	81.105	3.169	3.740
Sample 3	11.616	77.965	3.075	3.746
Sample 4	11.565	80.150	3.148	3.741

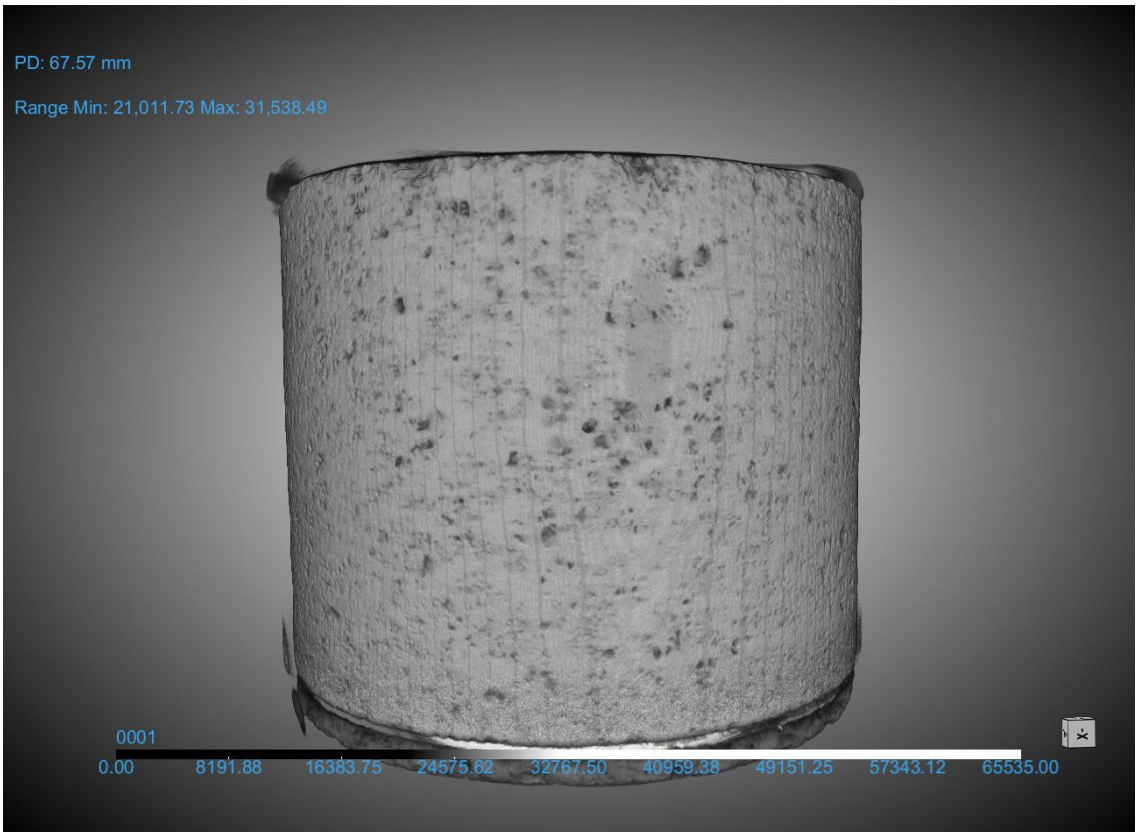


Figure 6a. Micro CT (Xradia) scan image of dry Sample 2, showing the pore space in the limestone plug before exposure to $scCO_2$.

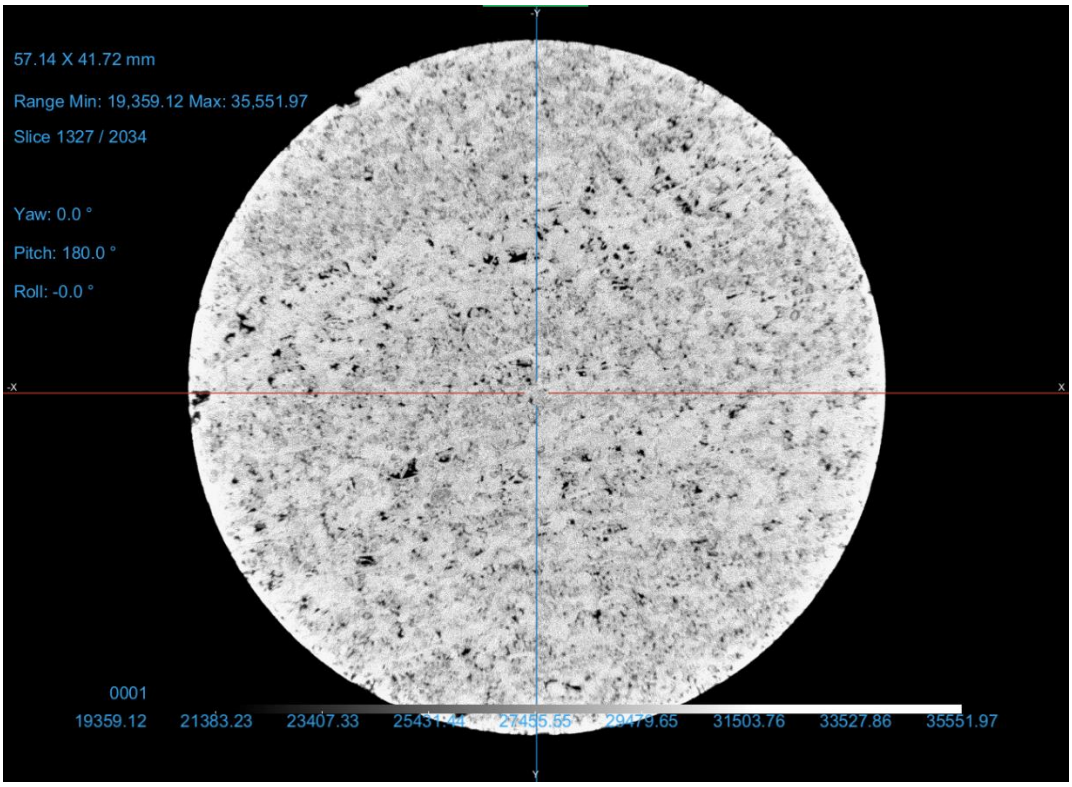


Figure 6b. Micro CT (Xradia) scan slice image of Sample 2, showing the pore space in the slice no 1327 out of 2034 before exposure to $scCO_2$.

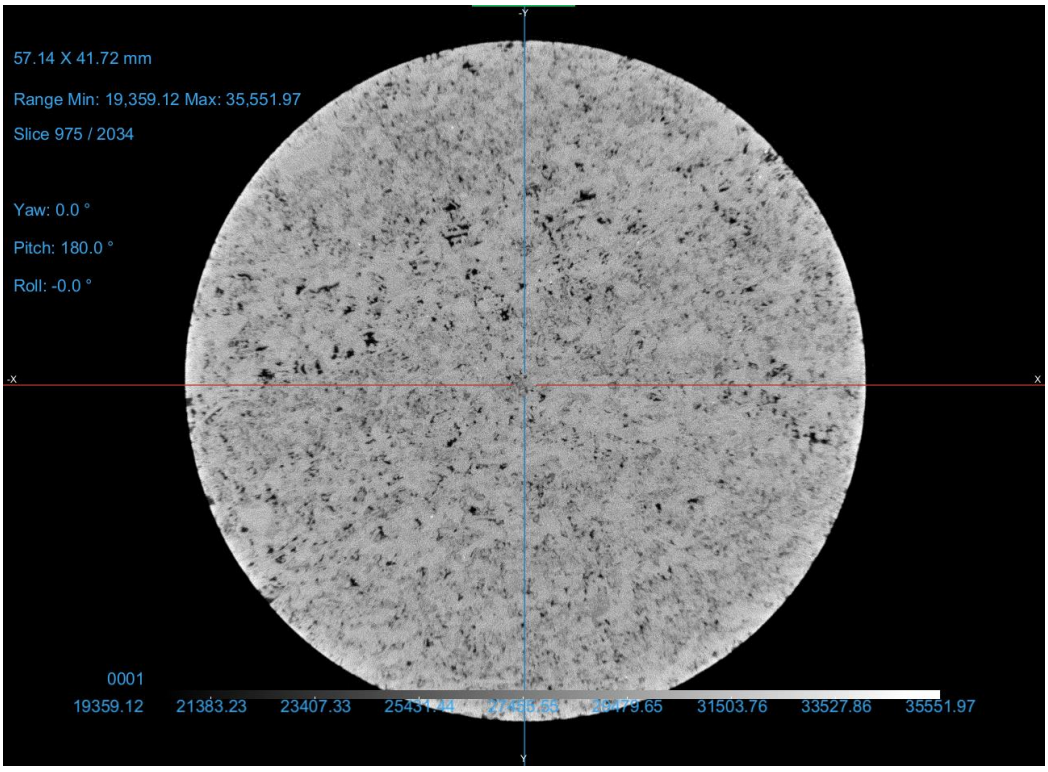


Figure 6c. Micro CT (Xradia) scan slice image of Sample 2, showing the pore space in the slice no 975 out of 2034 before exposure to $scCO_2$.

Figure 7a. Industrial CT scan image of dry Sample 3, showing the pore space in the limestone plug before exposure to $scCO_2$.

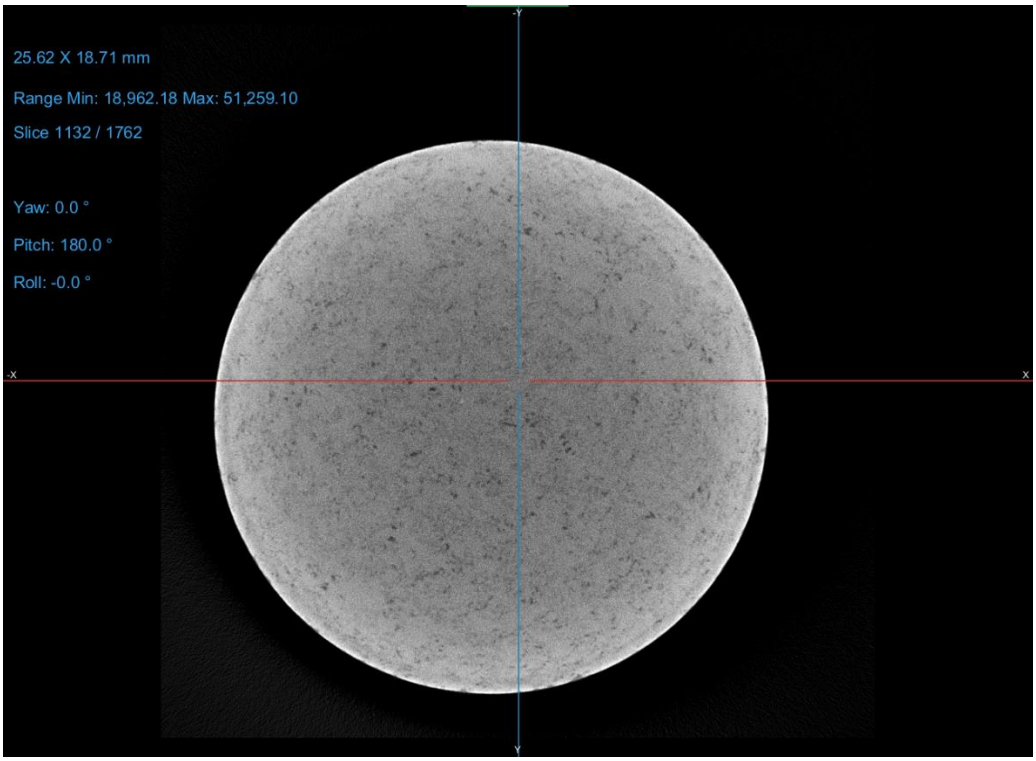


Figure 7b. Industrial CT scan image of dry Sample 3, showing the pore space in the slice no 1132 out of 1762 before exposure to $scCO_2$.

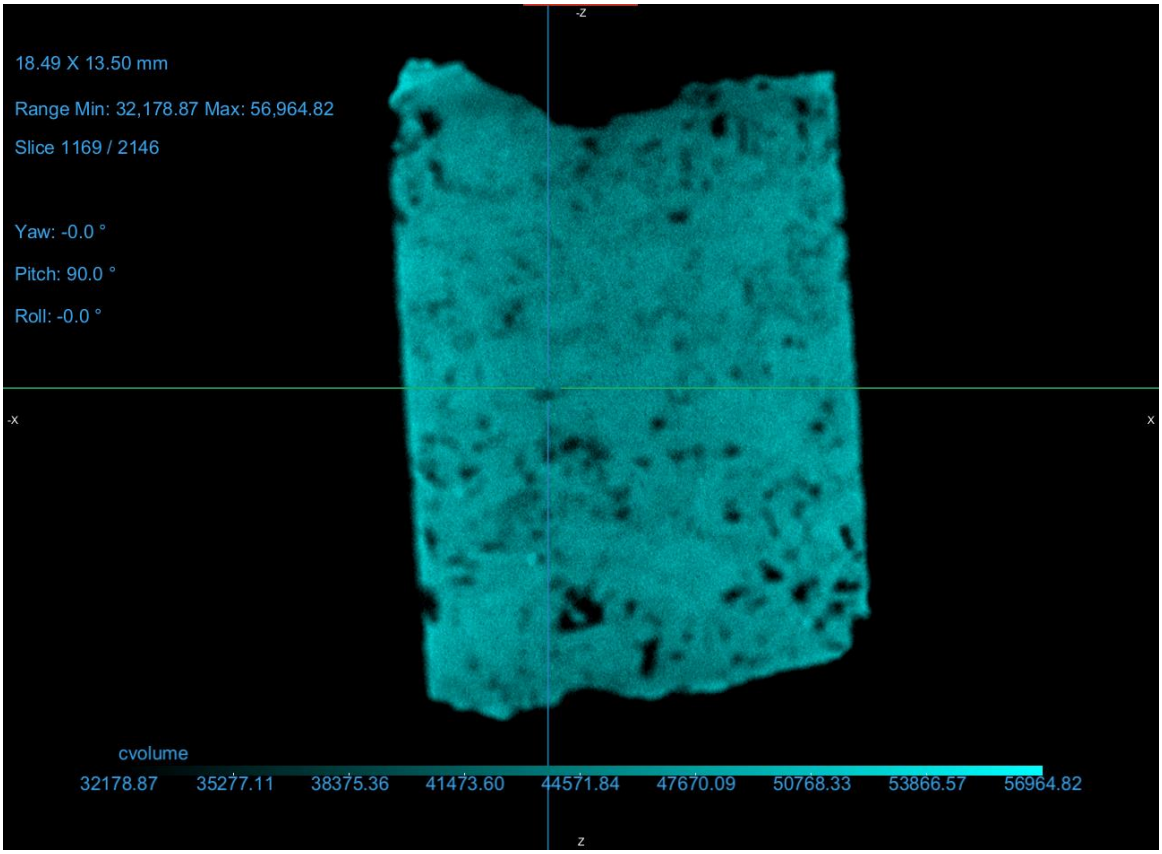


Figure 8 shows the industrial CT scan image of cutting sample 2, where the black spots represent pores and the colored spots indicate grains or rock.

The thin section images of before exposure to CO_2 of Indiana limestone under transmitted light and cross-polarized light are shown in Figure 9a and 9b.

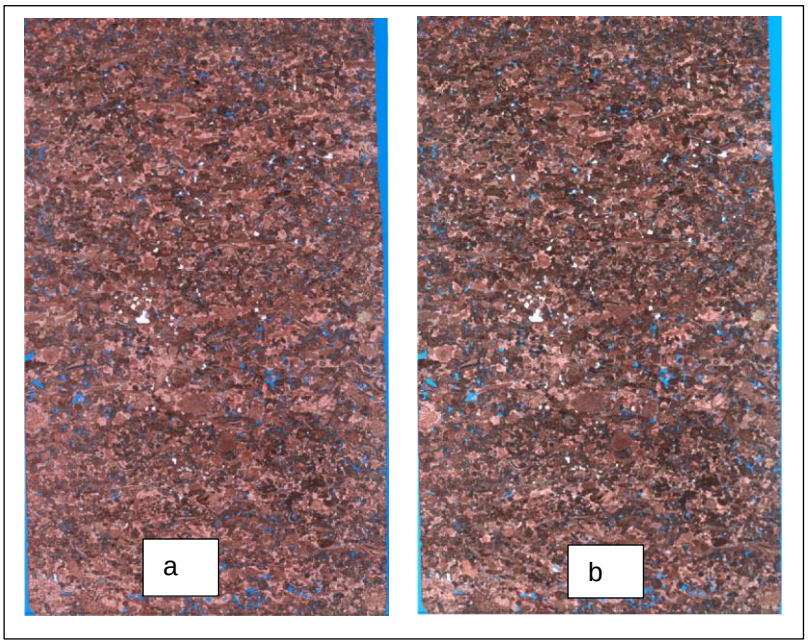


Figure 9a and 9b shows thin section images of before exposure to CO_2 of Indiana limestone under transmitted light and cross-polarized light.

The results of dielectric constant or dielectric dispersion with respect to frequency, both with and without bound water, are shown in Figures 10a and 10b before exposure to CO_2. After the samples were exposed to CO_2, the dielectric permittivity (or dielectric constant) was measured again as a function of frequency to characterize the vuggy and matrix pores in the carbonate system. This also serves as a validation of the geochemical and mineralogical changes induced by exposure to CO_2, brine, and rock in CO_2 sequestration projects, specifically in saline carbonate aquifers.

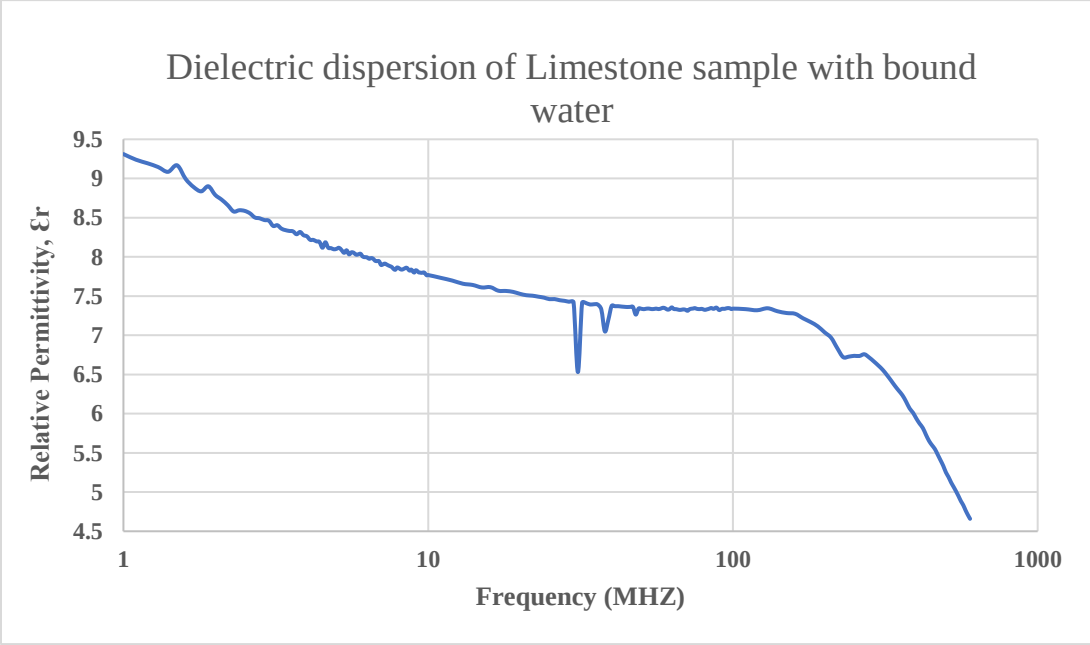


Figure 10a shows the dielectric dispersion of the limestone sample with bound water. A very high dispersion is observed in the dry sample, where the line is not constant. For a more consistent dielectric constant, the sample must have no bound water in the pores.

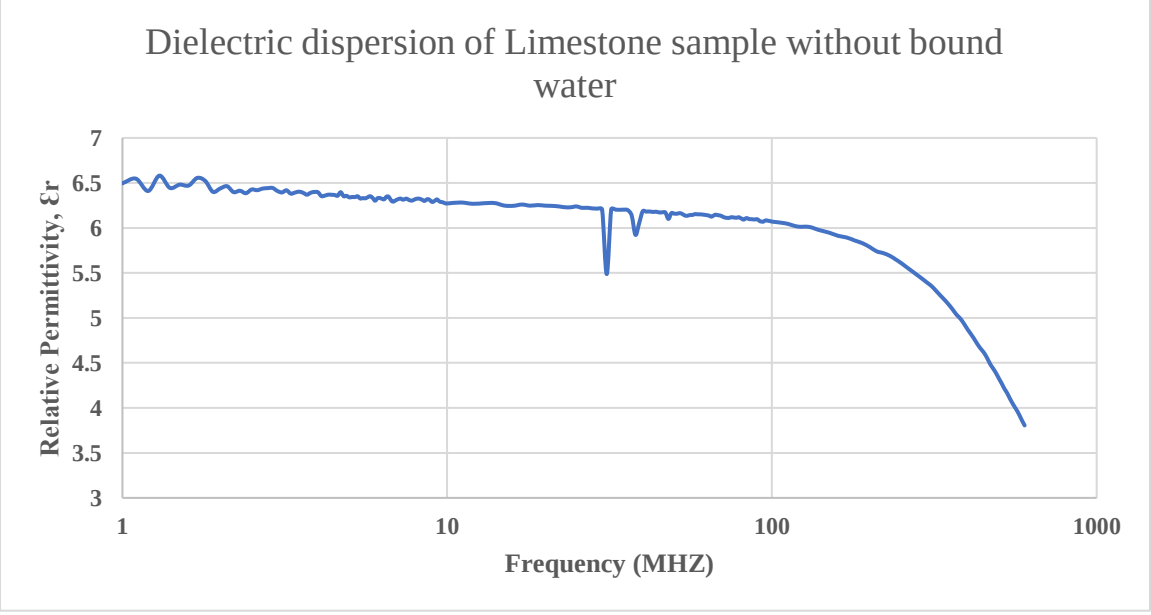


Figure 10b shows the dielectric dispersion of the limestone sample without bound water. A very low dispersion is observed in the dry sample, where the line is constant. For a more dispersion dielectric constant, the sample must have bound water in the pores.

Discussion

Khan, M., Siddiqui, S., and Thakur, G. (2024) investigated CO_2-brine-rock interactions, focusing on mineralization, precipitation, and dissolution (MPD) processes and their implications for long-term CO_2 storage. The study utilized a range of techniques, including thin section analysis, dual-energy CT scanning, reactive transport modeling, core flooding experiments, and static batch reactors, to explore the geochemical changes in the system. Petrophysical properties, such as dielectric dispersion, were measured before and after CO_2 exposure to quantify alterations in vuggy and intergranular (matrix) porosity in carbonate rock samples. Geochemical monitoring was conducted to track changes in the chemical composition of the rock and brine phases, providing a comprehensive understanding of the mineralogical transformations associated with CO_2 sequestration. The research also emphasized the importance of carbon security in ensuring the safe and effective long-term storage of CO_2 in saline carbonate aquifers.

(Cui *et al*., 2017) investigated the geochemical reactions in sandstone and carbonate reservoirs by exposing them to $scCO_2$ at conditions of 200 °C and 10 MPa. The study measured changes in mineral composition and ionic concentration to better understand the reaction mechanisms and quantify the kinetics of the reactions occurring under these conditions. Another study by (Moita *et al*., 2020) utilized a static batch reactor at a pressure of 8 MPa and a temperature of 40 °C under supercritical conditions. The experiment involved exposing mafic rocks to $scCO_2$-rich brine to investigate the geochemical and mineralogical changes. The aim was to explore the geochemical and mineralogical responses, with the findings from both experimental and modeling approaches over a 64-day period highlighting a dissolution mechanism.

Conclusion

In conclusion, this study explored in situ resistivity monitoring using the PLS 400 system during a 30-day exposure to $scCO_2$ and brine. Novel techniques were employed to investigate dielectric dispersion and dielectric permittivity, comparing conditions before and after CO_2 sequestration. The results validated geochemical changes by examining vuggy and matrix porosity. Furthermore, static batch reactor experiments were conducted using $scCO_2$-rich brine on ½ cm rock cuttings, with conditions set at 140 °F and 1500 psi, to observe changes before and after exposure. These changes were further analyzed through thin sections, micro CT, industrial CT, XRD, and SEM to examine grain and rock geochemical alterations. Through the application of these advanced techniques, we aim to enhance carbon capture monitoring technology, particularly for the Permian Basin. Looking forward, we plan to incorporate core samples from the Permian Basin into the DOE's CarbonSAFE II and CarbonSAFE III projects.

Acknowledgments

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